

“Some Physical Properties of Nickel Carbonyl.” By JAMES DEWAR, M.A., Sc.D., LL.D., F.R.S., Jacksonian Professor in the University of Cambridge, and HUMPHREY OWEN JONES, M.A., Fellow of Clare College, Jacksonian Demonstrator in the University of Cambridge. Received March 3,—Read March 26, 1903.

The properties of nickel carbonyl have until recently been the subject of but few investigations. Dr. Mond and his collaborators in the discovery of this remarkable substance determined some of its physical properties, including its boiling point, specific gravity, and vapour density. Subsequently Dr. Mond, in association with Professor Nasini, made observations on its molecular refraction and thermal expansion.

A substance of the peculiar molecular structure of nickel carbonyl seemed to call for further study. The investigation described in the present paper was carried out in the winter of 1901; the authors' intention being to make a complete study of the stability of the compound both in the gaseous and liquid conditions. While the work was in progress a paper by Mittasch was published\* containing an account of an admirable and exhaustive investigation of the velocity of the reaction between nickel and carbon monoxide, including the heat of formation and vapour tensions of the compound, covering part of the ground which we had examined. A number of interesting problems examined in the course of our inquiry however remain, which have not been touched upon by previous investigators, and to some of these the present paper is devoted.

The vapour density of nickel carbonyl was determined by Mond, Langer and Quincke† in air, at 50° C. by Victor Meyer's method. The value obtained was 86·7, while theory requires 85. The vapour density at this temperature is quite normal, and there is no evidence of association even at this temperature only some 7° C. higher than the boiling point of the compound. It was found that the vapour exploded at 60° C. with a flash of light, and carbon dioxide was detected among the products of decomposition. Berthelot‡ explained the explosion as being due to the production of carbon dioxide by the intermolecular reaction:—

$2\text{CO} = \text{CO}_2 + \text{C}$ , which was observed to take place when carbon monoxide acts on nickel at 350°—450° C. Later§ it was found that the action only proceeded in this way to a small extent, when

\* ‘Zeit. Phys. Chem.,’ 1902, vol. 40, p. 1.

† ‘Jour. Chem. Soc.,’ 1890, vol. 57, p. 749.

‡ ‘Compt. Rend.,’ vol. 112, p. 1343.

§ ‘Ann. Chim. Phys.,’ 1901 [7], vol. 22, p. 304.

nickel carbonyl vapour was decomposed. The reaction  $2\text{CO} = \text{CO}_2 + \text{C}$  liberates 38·8 kilogramme calories, so that if the heat of formation of nickel carbonyl is less than 77·6 kilogramme calories per molecule, this explanation would be valid. This condition is satisfied since Mittasch\* has shown that the heat of formation of nickel carbonyl is between 50·6 and 55·6 cal. Hence the detonation observed by Mond might result from the reaction :



The fact that nickel carbonyl was thus reported to be explosive, together with the explanation of its explosibility offered by Berthelot, strengthened the belief in its great instability and deterred experimenters from working with it, in any case at temperatures above its boiling point.

The authors observed that when nickel carbonyl was suddenly heated in an atmosphere of some inert gas, such as hydrogen or nitrogen, the vapour decomposed quietly with deposition of metallic nickel ; there was no explosion or flash of light, and the quantity of carbon dioxide produced was so small, in most cases, as to be almost negligible. This was found to be the case even when the temperature used was as high as 130° C. Mittasch\* states that he could detect no carbon dioxide when the compound decomposed below 100° C.

The explosion observed by Mond, Langer, and Quincke must therefore have been due to the presence of oxygen, and does not occur in its absence. The amount of carbon dioxide produced by the quiet decomposition is very small, so that the Berthelot reaction, though possible, only takes place to a very slight extent.

It was therefore clear that vapour-density determinations of the compound could be made in atmospheres of inert gases at temperatures much higher than 50° C. As vapour-density determinations of such a unique compound as nickel carbonyl under varying conditions would have a special interest and might well be expected to repay careful study, a large number of vapour-density determinations were made by Victor Meyer's method at temperatures between 63° C. and the boiling point of naphthalene (216° C.), in order to ascertain the effect of increasing temperature on the dissociation of the compound. The vapour-density apparatus was filled in different experiments with various dry inert gases, viz., hydrogen, nitrogen and ethylene, all carefully purified and especially freed from oxygen.

In order to trace the effect of the rapidity of gaseous admixture on the dissociation various forms of the vapour-density reservoir were employed. An atmosphere of carbon monoxide was employed to

\* *Loc. cit.*

investigate the effect of the gaseous product of dissociation on the stability of the carbonyl.

It was found that the rate of admixture of the vapour with the gases had a marked effect on the dissociation, as shown by the difference in the vapour densities, when taken under similar conditions, in the various inert gases; and, further, that the presence of carbon monoxide produced the expected diminution in the amount of the compound decomposed. In order to further confirm this, two reservoir tubes of different bore were used, one having a cross-sectional area about three times that of the other (the latter will be referred to as the narrow tube). In the latter, admixture could take place much less readily than in the former; consequently the surrounding gas would be expected to have a smaller effect on the extent of the dissociation. This was also confirmed by the experimental results; the vapour density in the narrow tube is almost independent of the gas employed.

The effect of the nature of the surface on the extent of dissociation was tested by using the tubes coated internally with a film of metallic nickel deposited from the vapour of nickel carbonyl by heating. The film of nickel seemed to bring about a state of equilibrium more rapidly, so that the vapour densities determined in these tubes were lower than those in the same tubes not covered by nickel (a similar effect was observed by Mittasch).

It was found that the rate at which the liquid evaporated, as would be expected in the case of a substance which readily dissociates, had some effect on the extent of the dissociation. Hence, it was necessary, in order to get comparable results, to arrange that approximately the same time was taken for vaporisation in all the experiments made at the same temperature. A definite end-point could be observed in each case at which the gas displaced by the vapour ceased to come off, and a much slower evolution of gas took place. The experiment was stopped when the more rapid evolution of gas gave place to the slower.

The results obtained are appended in the following table (Table I).

In the fourth column the percentages of nickel-carbonyl molecules dissociated are given, calculated from the formula  $P = \frac{85 - D}{3D} \times 100$ , where 85 is the theoretical vapour density of nickel carbonyl and D is the observed value.

Unless otherwise stated, it is to be understood that the determination was made in a Victor Meyer's apparatus of the usual type, occasionally referred to as the wide tube.

From the figures in the above table, it is seen that the value of the vapour density, deduced from the experiments in the wide tube, is greater in ethylene than in nitrogen and hydrogen. It was also

Table I.—Vapour Densities determined by Meyer's Method.

Temperature of the bulb. ° C.	Gas filling the bulb.	Vapour density found (H = 1).	Percent- age of Ni(CO) <sub>4</sub> dis- sociated.	Remarks.
63	Nitrogen .	83·3	0·7	Very slight deposit of nickel.
		78·2	2·7	Slight deposit of nickel.
64	Hydrogen	79·2		
66	Carbon monoxide	83·9	0·15	Nickel covered tube.
		85·2		
81	Nitrogen .	71·0	6·2	Slight deposit of nickel.
(Benzene)		72·1		
100	Hydrogen	67·3	8·8	Nickel deposited over several inches in the tube.
		67·0		
	„	56·9	16·7	Wide tube covered with nickel.
		56·7		
	„	79·0	2·4	Narrow tube. Nickel deposit extended about 32 cm.
		79·8		
„	Nitrogen .	70·8	6·7	
		70·9	..	Wide tube.
	„	75·6	4·1	Narrow tube.
„	Ethylene .	70·6	6·8	Wide tube. Nickel deposited over 2 cm. from bottom of tube.
		70·7		
		73·7	4·3	Wide tube. Moist nickel carbonyl. Nickel deposited irregularly over about 3 cm.
		76·7		
		77·8	2·7	Narrow tube. Nickel deposit extended 22 cm.
		79·5		
„	Carbon monoxide	85·0	0·39	Wide tube. No visible deposit of nickel.
		83·1		
		82·6	0·6	Wide tube, covered with nickel carbonyl, dried over phosphorus pentoxide.
		84·5		
		76·4	3·87	Narrow tube. Slight deposit of nickel.
		76·0		
110	Nitrogen .	48·4	25·4	Distinct deposit of nickel.
(Toluene)		48·1		
„	Carbon monoxide	75·2	4·4	Deposit of nickel scarcely visible.
		74·8		
129	Nitrogen .	25·1	76·5	Extensive deposition of nickel over tube.
(Amyl alcohol)		26·4		
	Carbon monoxide	31·7	54·5	„ „
		32·7		
135	Carbon monoxide	26·9	72·0	„ „
(Acetic anhydride)				
155	Nitrogen .	22·5	94·3	„ „
(Turpentine)		22·5		
	Carbon monoxide	23·2	..	„ „
		23·16	88·8	
182	Nitrogen .	23·3	89·0	„ „
(Aniline)		23·0		
	Carbon monoxide	24·4	82·8	„ „
		23·3	88·2	
216	Nitrogen .	22·4	93·0	„ „
(Naphthalene)		22·44		
	Carbon monoxide	(20·9)		
		21·3	99·7	

noticed that the deposit of nickel in the latter two gases extended higher up the tube than in the former, and was higher in hydrogen than in nitrogen. In carbon monoxide, on the other hand, the vapour density is higher than in the gases hydrogen, nitrogen, or ethylene, the values at 100° C. being nearly normal, and the dissociation was incomplete even in aniline vapour. This demonstrates very clearly the effect of the presence of one of the dissociation products on the amount of the dissociation.

In the narrow tube, however, the values obtained at 100° C. do not seem to depend, to any great extent, on the nature of the surrounding gas, the values in carbon monoxide and in the inert gases being almost identical, which shows the great effect of rate of admixture and diffusion on the dissociation.

The amount of dissociation increases rapidly with the temperature; in nitrogen at 155° C. it is practically complete. The rate of increase in carbon monoxide is distinctly slower, the difference between the vapour densities in nitrogen and carbon monoxide at 129° C. being quite marked. Above 155° C. the results obtained are somewhat irregular; but dissociation seems to be nearly complete at atmospheric pressure, since only a small deposit of nickel could be obtained when the tube was placed horizontally and a clear part heated with the blowpipe.

A few vapour-density determinations were also made by Hoffmann's method at temperatures between 17° C. and the boiling point of aniline (182° C.) in order to observe the dissociation of the undiluted vapour. Complete dissociation is practically reached at 182° C., but even then the application of a pointed flame to a clear portion of the tube produced a slight deposit of nickel, so that traces of nickel carbonyl were still present.

The results are given in the appended table (Table II).

The results of the experiments in the narrow tube are given in the fifth column for the sake of comparison, the phenomena in this case being practically the dissociation of the vapour in contact with its own dissociation products. The dissociation is clearly greater under reduced pressure, as might be anticipated.

The general results of the vapour-density determinations are readily seen from the curves in fig. 1 (p. 433).

Having thus found that the vapour of nickel carbonyl was much more stable at elevated temperatures than had hitherto been suspected, we resolved to examine the stability of the liquid under pressure, and if possible make observations on it as far as its critical point.

Small sealed tubes, from one-half to one-third full of nickel carbonyl, were heated to 200° C. without bursting. A small quantity of nickel was deposited on the first heating, and it was found that its quantity was not appreciably increased on repeating the operation. On

standing a sufficient length of time at the ordinary temperature the nickel gradually dissolved again, although it was covered by the excess of liquid. This proved in an interesting manner the ease with which the reaction between the deposited nickel and carbon monoxide is reversible.

The amount of the nickel deposition was notably greater when the liquid was heated in contact with mercury, so that the use of the Cailletet pump for the examination of the critical phenomena was not practicable.

Rough measurements of the critical temperature were made by observing the temperature at which the meniscus disappeared and

Table II.—Vapour Densities of Nickel Carbonyl by Hofmann's Method.

Temperature of bath.	Vapour density.	Pressure in mm. of mercury.	Percentage of nickel carbonyl dissociated.	Percentage dissociated at atmospheric pressure.			
				In nitrogen.	In carbon monoxide.		
° C.							
17	85·6	67·7	0·0				
35	81·8	161·4	0·13				
(Ether)							
78	62·6	217·8	11·9	4·1 at 100° C.	3·87 at 100°		
(Alcohol)				in narrow tube	in narrow tube		
129	25·2	389·4	79·1	{ 76·5	54·5		
(Amyl alcohol)	23·8	365·6	85·7			wide tube	wide tube
182	21·5	349·0	98·4				
(Aniline)	20·8	320·6	..	Practically complete in wide tube.			
	21·7	356·0	95·7				

reappeared, when a quantity of the liquid was alternately heated and cooled in an exhausted and sealed off piece of glass tube of 2—3 mm. bore. The tube was heated side by side with a thermometer in a glycerine bath, and was so arranged that it could be inverted at will. The temperatures at which the meniscus disappeared and reappeared in the course of many repeated observations with different samples of material, ranged between 191° C. and 195° C.

It appears from the observations made with such tubes that the most reliable results were obtained the first time they were heated, the meniscus being better defined and disappearing more sharply than on subsequent occasions. The blurred effect noticed on a repetition of the experiment is due to a somewhat greater amount of carbon monoxide being present.

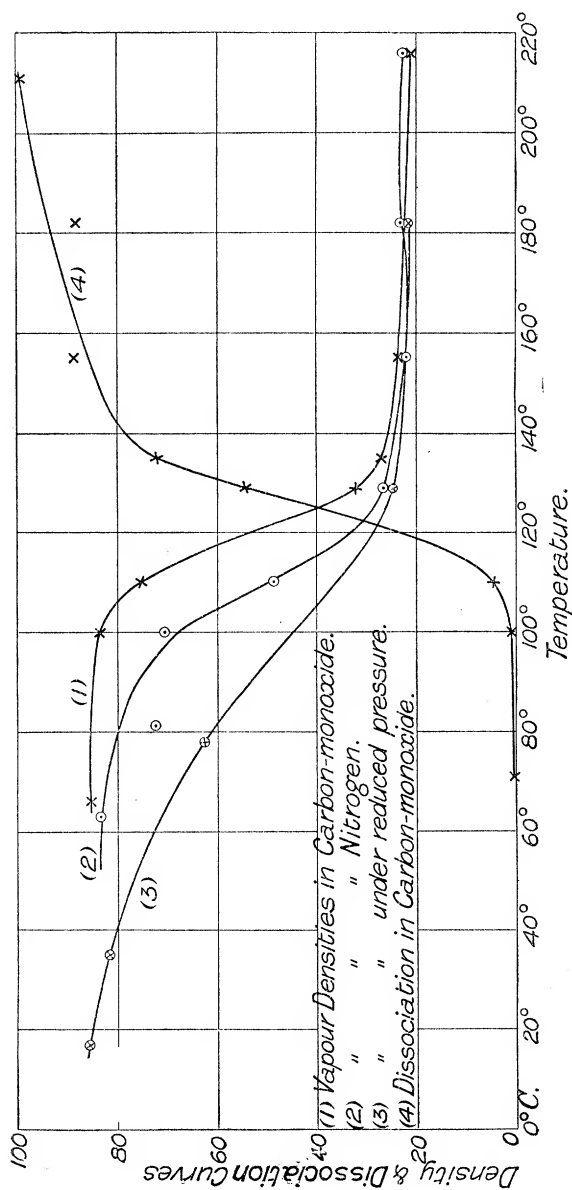


FIG. 1.

The presence of carbon monoxide would be expected to cause a lowering of the temperature at which the meniscus disappeared, and this expectation was realised in the course of the experiments. Hence the temperature observed in the first experiment is probably below the

true critical temperature. The presence of 4—5 per cent. of carbon monoxide with its low critical temperature  $128^{\circ}$  abs. would be expected to lower the temperature at which the meniscus disappears by about  $5^{\circ}$  C. That this quantity of carbon monoxide might be present at any time is shown by the following experiment:—

Volume of tube, 1.35 c.c.

„ nickel carbonyl left after heating to  $193^{\circ}$  C. = 0.437 c.c.

Amount of nickel deposited = 0.0147 gramme.

„ carbon monoxide liberated = 0.0284 gramme = 5.02 per cent. of the residual nickel carbonyl.

Hence it is very probable that the true critical temperature is about  $200^{\circ}$  C.

Comparative experiments made with pure ethyl ether in similar tubes, gave a critical temperature of  $193^{\circ}$  C. The accepted value for the critical temperature for ether being  $194^{\circ}5$  C., the observed temperature for nickel carbonyl cannot be far removed from the correct value.

The formula  $T_b = 0.66 T_c$ , where  $T_b$  is the absolute boiling point and  $T_c$  the absolute critical temperature, should be applicable to the case of nickel carbonyl since it is applicable to ether, a liquid which has a critical temperature of approximately the same value. Taking the boiling point to be  $43^{\circ}3$  C., the critical temperature calculated from the above relation would be  $201^{\circ}4$  C., which agrees very well with the value which was found as a probable minimum critical temperature.

Although it had not been surmised that nickel carbonyl could ever stand heating above  $100^{\circ}$  C., nevertheless Mond and Nasini\* calculated the hypothetical critical temperature of nickel carbonyl from the results of their experiments on its coefficient of expansion by means of a formula given by Thorpe and Rücker and found the value  $151^{\circ}$  C. In a similar manner Ramsay and Shields† calculated the critical temperature from the temperature coefficient of the molecular surface energy. The value deduced in this way is  $182^{\circ}8$  C. It therefore appears that the hypothetical critical temperature calculated by either of these methods falls considerably below its actual value.

Rough indications of the critical pressure were obtained by introducing into the sealed tube containing the nickel carbonyl a small tube of very fine bore, closed at one end and having a small globule of mercury introduced at the other, to act as a manometer. The position of the globule was observed at the ordinary temperature, and again at the critical point. The volume of the air in the small tube occupied about one-thirtieth of its original volume at the latter

\* 'Zeit. Phys. Chem.,' 1891, vol. 8, p. 150.

† 'Jour. Chem. Soc.,' 1893, vol. 63, p. 1108.



temperature, so that the pressure in the tube seems to be rather more than 40 atmospheres at the critical point. On cooling, the indicating globule remained permanently displaced some distance up the tube, showing the existence of a pressure developed by the decomposition of the nickel carbonyl. On standing for some time the whole of the nickel disappears, and the carbonic oxide pressure disappears.

The pressure on cooling seemed to be about ten atmospheres, hence the critical pressure would be about thirty atmospheres. Later it will be shown that this is near the actual value.

The critical constants of the compound being known, together with the boiling point, it is possible to calculate a vapour-pressure curve. It was, however, thought better to determine the vapour pressure at a number of temperatures below the boiling point of the liquid, by the static method, and from this curve by extrapolations to deduce the values for higher temperatures.

A wide barometer tube (about 0·7 cm. diameter) was carefully cleaned, dried, and drawn off to a fine capillary tube at one end. The tube was then placed upright in a vessel of pure dry mercury and exhausted thoroughly with a Fleuss pump. A small tube full of nickel carbonyl was now introduced at the bottom of the tube and the whole then exhausted again, while surrounded by a freezing mixture, in order to get rid of all adhering air, and finally sealed off rapidly at the fine capillary. By this method of procedure only a very small amount of decomposition took place during the sealing off, as indicated by the very slight deposit of nickel. The pressure was then read off by means of a kathetometer, while the tube was surrounded by a bath kept at various constant temperatures.

The results are appended below, together with those obtained by Mittasch\* by the dynamic method.

Dewar and Jones.		Mittasch.	
- 9° C.	94·3 mm.	2°·05 C.	133·1 mm.
- 7	104·3	7·5	170·5
- 2	129·1	15·27	238·2
0	144·5	20·2	294·3
+ 10	215·0	24·26	349·7
+ 16	283·5	29·52	444·2
+ 20	329·5	34·29	532·6
+ 30	461·9	39·97	647·2

The values for - 9° C. and + 30° C. give the following Rankine formula for the relation between the pressure  $p$  in millimetres of mercury and the absolute temperature  $T$ .  $\log p = 7·355 - 1415/T$ . At 200° C. (about the critical temperature) the pressure calculated from this equation is 30·4 atmospheres. Taking the results obtained

\* *Loc. cit.*

by Mond and Nasini, viz., the boiling point  $43^{\circ}\text{C}$ . 751 mm. and the pressure at  $20^{\circ}\text{C}$ . 338.7 mm., a similar expression,  $\log p = 7.281 - 1392/T$ , is obtained.

Taking Mittasch's pressures for  $2^{\circ}\text{C}$ . and  $40^{\circ}\text{C}$ . the Rankine obtained is :—

$$\log p = 7.781 - 1555.7/T.$$

The boiling points calculated from these formulæ are given below :—

Mond.....	$43^{\circ}.3\text{ C}$ .
Mittasch .....	$44^{\circ}.4$
Dewar and Jones .....	$43^{\circ}.2$

In order to further confirm our vapour-pressure determinations, we made a determination of the boiling point of some carefully dried and redistilled nickel carbonyl. With the barometer at 769 mm. the liquid boiled at  $43^{\circ}.2 - 43^{\circ}.33\text{ C}$ .

It would therefore appear that our vapour tension curve is the more accurate. The following curves, fig. 2, illustrate very clearly the extent of the deviations at different temperatures.

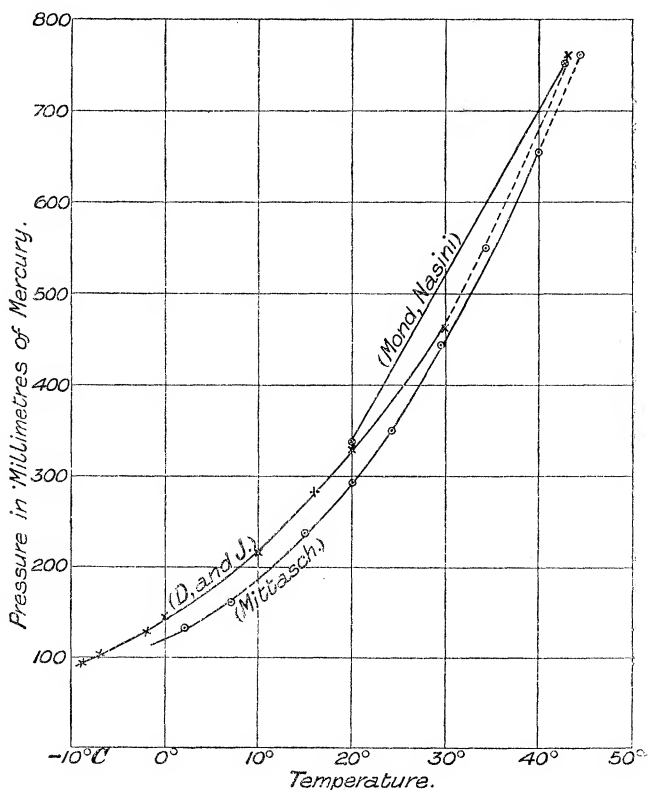


FIG. 2.

The latent heat of vaporisation of  $\text{Ni(CO)}_4$ , is 38.1 calories per gramme, and the Trouton constant (molecular latent heat divided by the absolute boiling point) is 20.6, its value for ether being 22. The number obtained by dividing the absolute critical temperature by the critical pressure, which is proportional to the volume of the molecule, Van der Waal's constant  $b$ , is 15.5; the similar number for carbon monoxide is 3.7, so that nickel carbonyl according to theory has a molecule 4.2 times larger than carbon monoxide. The molecular volume of nickel carbonyl at its boiling point is 136, as compared with 110 for ether. The critical density appears to be about 0.46, while that of ether is only 0.25. If the liquid densities of Mond and Nasini\* are taken with the critical data, then the Waterston formula  $v = 2.0398 - 0.5667 \log (198.7 - t)$  fits in very well with the results. A similar formula for ether given by Avenarius is:—

$$v = 3.19 - 0.802 \log (191 - t).$$

The molecular volume of nickel carbonyl at its boiling point is 136; subtracting from this 7.2 for the nickel atom, we have 32.2 as the volume of each molecule of carbon monoxide in the molecule. Now liquid carbon monoxide at its boiling point has the molecular volume of 35, so that contraction would take place if liquid carbon monoxide could combine with nickel. The heat of formation of nickel carbonyl is about four times greater than that of the liquefaction of the equivalent amount of carbonic oxide under normal conditions.

The experiments described above show clearly that nickel carbonyl is a substance admirably suited for the demonstration of the phenomena of dissociation. Great care must, however, be taken in handling the substance, owing to its poisonous properties when inhaled. It also forms an excellent illustration of a reversible reaction, and the following experiments serve to illustrate the way in which it may be used for this purpose.

A number of carefully dried tubes were exhausted by means of a Fleuss pump, and were then filled with a mixture of 10 per cent. nickel carbonyl vapour and 90 per cent. carbon monoxide, at pressures of 50, 100, 226, 304, 396, 504, and 624 mm. of mercury respectively. These tubes were then heated in a bath until nickel began to deposit; the tube under observation was then kept at that or a slightly higher temperature for about half-an-hour, and afterwards tested for the presence of nickel carbonyl by heating a clean portion of the tube with a fine pointed flame, and in this way the presence of even a very small trace of nickel carbonyl was immediately detected by the formation of a bright mirror of nickel on the hot part of the tube. The tube at 50 mm. pressure did not deposit nickel when placed in alcohol vapour,

\* *Loc. cit.*

but did so at  $100^{\circ}\text{C}.$ , and, after heating for a few hours at this temperature, no nickel carbonyl could be detected in the tube. After standing for a few days, however, nickel was deposited when a clean portion of the tube was heated with a pointed flame, thus showing that nickel carbonyl had been regenerated. In the 100 mm. tube nickel was still deposited after heating for two days at  $100^{\circ}\text{C}.$ ; all the nickel carbonyl was found to have disappeared after the tube had been heated for some time to  $130^{\circ}\text{C}.$  Nickel was deposited in the tube at 226 mm. pressure at  $130^{\circ}\text{C}.$ , in the 301 mm. tube at  $158^{\circ}\text{C}.$ , and in the other tubes at slightly higher temperatures. In the two tubes at the highest pressures there was a considerable quantity of the carbonyl present after heating for an hour at  $160^{\circ}\text{C}.$  All the tubes in which the nickel carbonyl had been so far destroyed that no visible deposit of nickel could be obtained on heating a clean portion of the tube with a small flame, after standing for a few days contained enough of the carbonyl to be readily detected by the above test.

Another form of experiment suitable for demonstration proved the reaction proceeded rapidly at the ordinary temperature, and with a measurable velocity at low temperatures, even when the pressure of the carbonic oxide atmosphere was below 200 mm. A large bulb of about 200 c.c. capacity was connected to a mercury manometer of small bore (so that the movements of the mercury in the manometer were proportional to the changes of gas concentration in the bulb). The bulb was highly exhausted and then filled with pure nickel carbonyl vapour to a pressure of 51 mm. of mercury at  $15^{\circ}\text{C}.$  After heating for about an hour to  $100^{\circ}\text{C}.$  the pressure, measured after cooling, had risen to 143 mm., corresponding to a decomposition of about 60 per cent. of the nickel carbonyl present. Heated in a glycerine bath to  $154^{\circ}\text{C}.$  the pressure reached 198 mm., corresponding to practically complete decomposition, which ought to develop a total pressure of 204 mm.

On rapidly cooling the bulb and allowing it to stand at the ordinary temperature the pressure fell, at first, about 3.2 mm. in an hour, then after two days it had fallen to 120 mm., or about 55 per cent. had recombined, after four more days the pressure was 97 mm., or about 60 per cent. had recombined, after standing four weeks some of the deposited nickel remained unattacked.

The bulb was again heated to  $150^{\circ}\text{C}.$ , so as to deposit all the nickel on the lower part of the tube, and the pressure now rose again to 200 mm. The lower part of the bulb where the nickel had deposited, was now immersed in liquid air, when it was observed that still a small but distinct diminution in pressure took place after some hours. Liquid carbonic oxide did not, however, appear to react with nickel reduced from the oxide by hydrogen.

The volatile iron carbonyl has been made the subject of a number of similar observations, dealing with its physical properties and chemical stability, which will be discussed in another communication.

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“An Enquiry into the Variation of Angles observed in Crystals, especially of Potassium-Alum and Ammonium-Alum.” By Professor H. A. MIERS, M.A., D.Sc., F.R.S. Received March 10,—Read March 26, 1903.

(Abstract.)

Corresponding angles measured on different crystals of the same substance usually differ slightly. On cubic crystals the theoretical angles are known. Pfaff professed to have established that only those cubic crystals which display birefringence exhibit divergence from the theoretical angles, but Brauns showed that in lead nitrate, ammonia-alum, and spinel, for both isotropic and birefringent crystals alike, the octahedron angle may differ by as much as  $20'$  from that of the regular octahedron.

The author has endeavoured to trace the changes of angle upon one and the same crystal during its growth by measuring it at intervals without moving it from the solution in which it is growing. This is accomplished by means of a new telescope-goniometer in which the crystal is observed through one side of a rectangular glass trough, and the changes in the inclination of each face are followed by watching the displacements of the image of a collimator slit viewed by reflection in it. The crystal is held by a platinum clip which it envelopes as it grows. Small movements of the image are followed by means of a special micrometer-eyepiece which accurately measures the magnitude and direction of the displacement.

Examined in this way an octahedron of alum (ammonium or potassium) is found to yield not one but three images from each face; and closer inspection shows that the crystal is not really an octahedron, but has the form of a very flat triakis octahedron. It often happens that of the three faces which nearly coincide, one is large and the remaining two very small, so that of the three images one is bright and the others are very faint, and can only be discerned with difficulty; in such a case the crystal as measured in the ordinary way would appear to be an octahedron whose angle differs from the theoretical value by a few minutes.

When a growing crystal of alum is watched for several hours or days, it is found that the three images yielded by an apparent octahedron face continually change their position; one set fades away and is replaced by another set, which are generally more widely